PTO 09-1674

CC=NL DATE=19790621 KIND=A
PN=7714035

METHOD OF PRODUCING POLYVINYL ALCOHOL
[WEWRKWIJZE TER BEREIDING VAN POLYVINYLALCOHOL]

ROBERT C. TUYT, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. December 2008

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	NL
DOCUMENT NUMBER	(11):	7714035
DOCUMENT KIND	(12):	A
PUBLICATION DATE	(43):	
APPLICATION NUMBER	(21):	7714035
APPLICATION DATE	(22):	19771219
INTERNATIONAL CLASSIFICATION	(51):	C08F 16/06; C08F 8/12
PRIORITY COUNTRY	(33):	NA
PRIORITY NUMBER	(31):	NA
PRIORITY DATE	(32):	NA
INVENTOR(S)	(72):	Robert C. Tuyt, Pieter J. Lemstra, and Gezinus Kremers
APPLICANT(S)	(71):	STAMICARBON B.V.
DESIGNATED CONTRACTING STATES	(84):	NA
TITLE	(54):	METHOD OF PRODUCING POLYVINYL ALCOHOL
FOREIGN TITLE	[54A]:	WERKWIJZE TER BEREIDING VAN POLYVINYLALCOHOL

Description

/1*

The invention concerns producing polyvinyl alcohol by solvolysis of polyvinyl acetate catatalyzed with alkali.

Polyvinyl alcohol cannot be directly produced by polymerization of vinyl alcohol, which is tautomeric with acetaldehyde. Usually polyvinyl alcohol is produced by reaction of polyvinyl acetate catalyzed with alkali or acid, so-called alcoholysis. Normally, hydrolysis, that is, reaction with water, is also possible. Therefore the term solvolysis, that includes both alcoholysis and hydrolysis, is preferred here. The solvolysis can take place completely, that is at least 99%, but also incompletely. Then, polyvinyl acetates that are partially solvolyzed are obtained. For the most part, the degree of solvolysis is more than 70 mol%, but solvolyzed polyvinyl acetates with solvolysis degrees of less than 70 mol% and even less than 40 mol% are also known. These can be considered as copolymers of vinyl acetate and vinyl alcohol, but it is generally useful to designate all of them as polyvinyl alcohols.

Polyvinyl alcohols are used in the textile and paper industry and as emulsifiers and suspension agents and protective colloid in the case of emulsion and suspension polymerization. Polyvinyl alcohols with solvolysis degrees of at least 70 mol% are water-soluble; those with a degree of solvoylsys of less than 70 mol% are insoluble or very poorly soluble in water. With a decreasing degree of solvolysis the solubility decreases rapidly. If the solvolysis degree is less than 40 mol%, then

*Numbers in the margin indicate pagination in the foreign text.

they are soluble in polar organic solvents such as alcohols. Polyvinyl alcohols with solvolysis degrees of 40-70 mol% are soluble in alcohol-water mixtures, and poorly soluble or insoluble in water and in alcohol.

It is known that polyvinyl alcohols with solvolysis degrees of less than 70 mol% can be used as suspension media in the case of suspension polymerization, in particular suspension polymerization of vinyl chlorides, together with water-soluble suspension agents. They are called secondary suspension agents. Polyvinyl alcohols of this kind are very expensive and therefore the application has been limited up to now.

The production of polyvinyl alcohols with solvolysis degrees of less than 70 mol%, as opposed to those of polyvinyl alcohols with solvolysis degrees of more than 70 mol%, presents many problems. In general the solvolysis is carried out by dissolving polyvinyl acetate in a lower /2
alcohol and then solvolyzing it at a somewhat higher temperature by means of acid or alkaline catalysts. The viscosity of the solution increases greatly in the case of the production of solvolysis degrees of 30 to 50 mol% and a gel appears in the case of solvolysis degrees of 50 to 70 mol%. If the solvolysis degree increases above 70 mol%, then the polyvinyl alcohol can be precipitated as a white powder by vigorously stirring and the liquid phase becomes less viscous again. Treating polyvinyl alcohols with solvolysis degrees above 70 mol% therefore is not a problem, but the production and treatment of the lower solvolyzed polyvinyl alcohols in the form of very viscous solutions or gels is possible. For lack of better, viscous solutions of this kind or gels are treated by heating with stirring

in order to evaporate the solvents, such as alcohols and/or esters. This is an uneconomical method since the polyvinyl alcohols persistently bind the solvent and the diffusion path of the solvent molecules is long. The treatment therefore lasts noticeably longer than the solvolysis.

Whenever an attempt is made to dry more rapidly by heating to higher temperatures, decomposition takes place, which goes along with discoloration and reduction of solubility.

Another difficulty is that inhomogeneous products are obtained. The solvolysis is ended by neutralization of the catalyst. In very viscous solutions or in gels, it is difficult or impossible to end the solvolysis at the desired value. The neutralization agent for the catalyst cannot be rapidly mixed homogeneously with the solvolyzed reaction product and therefore the solvolysis cannot be rapidly ended homogeneously. This is more difficult since the solvolysis rate reaches a maximum value precisely in the gel phase and is noticeably greater than the solvolysis rate of solvolysis degrees lower than 40 mol% or greater than 70 mol%. Consequently a polyvinyl alcohol with a wide degree of solvolysis is obtained.

It appeared that for a number of applications of polyvinyl alcohols with a solvolysis degree of less than 70 mol%, in particular of 40-70 mol%, a small degree of solvolysis distribution is precisely of interest. For polyvinyl alcohols with a higher solvolysis degree a small distribution of the solvolysis degree is known from Dutch Patent Application 268,248. This method is not suited for producing with a solvolysis degree of /3

less than 70 mol% and a small solvolysis degree distribution. Namely, the solvolysis reaction may be allowed to run, because inhomogeneous products can be obtained in the case of stopping by neutralization of the catalyst. In order to let the solvolysis end in the case of a low solvolysis degree of less than 70 mol%, less catalyst may be used, but in this case the reaction proceeds slowly and the difficulties in treatment are not resolved.

It has now been found that polyvinyl alcohols can be produced by solvolysis of polyvinyl acetate catalyzed with alkali to a solvolysis degree of 40-70 mol% by conducting solvolysis in a solvent mixture of an alcohol with 1-4 carbon atoms and 2-30 parts by weight of water per 100 parts by weight of alcohol.

For this the polyvinyl acetate is dissolved in alcohol, for example methanol, ethanol, propanol, isopropanol, butanol, isobutanol, preferably in methanol or ethanol, in particular in methanol, and then water and alkaline catalyst are added. Preferably the catalyst, for example potassium or sodium hydroxide, is dissolved in the amount of water necessary for producing the solvent mixture, and then this solution is mixed with the mixture of polyvinyl acetate in methanol. The concentration of the polyvinyl acetate in the solvent mixture can vary within wide limits. The maximum usable concentration depends on the circumstances and on the polymerization degree of the polyvinyl acetate. The greater this is, the more viscous the solutions should become, but these are preferably not so viscous that they are difficult to use. In most cases concentrations of 20 to 25% by weight are usable. When the polymerization degree is smaller

than 1000, even higher concentrations of 50% or more are still well usable. As a result of the solvolysis the viscosity does not increase, or increases only slightly, on the other hand the solvolysis carried out in alcohol, in particular the viscosity increasing very greatly.

The polyvinyl alcohols according to the invention are particularly suited for being used as secondary suspension agents in the case of the suspension polymerization of vinyl chloride.

The difficulties in ending solvolysis and treating polyvinyl alcohols in the case of solvolysis degrees of less than 70 mol% are /4
indicated in American patent specification 3,552,933, in which it is proposed that a neutralization agent for the catalyst and 5 to 55% by weight of water, calculated from the reaction mixture, be added and rapidly mixed in producing the desired solvolysis degree. This does not appear to be able to stop the existing difficulties completely. It is true that the treatment is facilitated, but the solvolysis degree distribution remains wide. The dilution of the gel phase requires time and neutralization in particular still proceeds slowly in the gel portion.

The solvolysis to solvolysis degrees of 30 to 65 mol% is completely carried out in the gel phase according to Netherlands patent application 77 00 836 in a solvent mixture of 50-98 vol% of a non-polar organic solvent. A polyvinyl alcohol having a block structure of acetate and hydroxyl groups is obtained. The application gives no indications of how the solvolysis is ended in the gel phase.

In the case of the present method the viscosity of the solutions increases little or not at all in the case of solvolysis degrees of 40 to 70 mol% and no gels are formed. This makes the treatment easy. In addition, the solution of polyvinyl alcohol and water can be used for application as a secondary suspension agent in such a way that treatment can be completely omitted. The byproducts such as catalyst residues and so forth are not a problem.

Surprisingly it also appeared that the solvolysis can be regulated by the choice of the amount of water with respect to the polyvinyl acetate used as the starting point and the alcohol-water ratio. The solvolysis rate appears to be small in the case of the present method in the case of a specific solvolysis degree. In the case of the neutralization of the catalyst, few differences in the solvolysis degree should arise, even when the neutralization does not rapidly proceed homogeneously. In all cases a small solvolysis degree distribution is obtained in this way.

Preferably methanol or ethanol, more preferably methanol, is used as alcohol in which the solvolysis is carried out. The amount of water is preferably 5-20 parts by weight per 100 parts by weight of alcohol. The solvolysis can be carried out at temperatures from 0°C to the boiling point of the system. Preferably the temperature is at least 10 and in general it is chosen to be ho higher than 50°C. An alkali metal hydroxide, for example sodium or potassium hydroxide or an alkali metal - alcoholate, for example sodium or potassium methylate in amounts of 0.1 to 2 % /5

by weight, preferably 0.5 to 1 % by weight calculated on the weight of the polyvinyl acetate, is used as the catalyst. The mixture is stirred well during the solvolysis.

The production of the polyvinyl alcohols under consideration preferably starts from a polyvinyl acetate with a polymerization degree of at least 350 and at most 2000, more particularly at least 500 and at most 1500, although the invention is not limited to this, since polyvinyl alcohols are obtained even in the case of solvolysis of polyvinyl acetate with a polymerization degree of less than 350 or respectively more than 2000 polyvinyl alcohols with a small solvolysis degree distribution.

The solvolysis is ended by adding an acid such as hydrochloric acid, sulfuric acid, acetic acid with good stirring. Acetic acid, which can be added as glacial acetic acid, if required, diluted with an alcohol, in particular methanol, is particularly suitable.

Polyvinyl alcohols according to the invention also can be produced by starting with polyvinyl esters of other carboxylic acids, for example polyvinyl priopionate, polyvinyl butyrate, and so forth. Inasmuch as these are less current and lasting products than polyvinyl acetate, preference should be given to polyvinyl acetate as a raw material. In a modification of the cost-price ratios, for technical reasons there is no problem in starting from another polyvinyl ester.

The invention is illustrated by the following examples, without being limited thereby.

Examples 1-4

In a double-walled reaction, 100 parts by weight of polyvinyl acetate having a polymerization degree dP = 600 are dissolved in methanol with gentle warming. Then 0.8 % by weight of potassium hydroxide, calculated with respect to the polyvinyl acetate, dissolved in water, is added and the mixture is held at 40°C. The solvolysis is ended after 1, respectively 2, respectively 3 hours by adding an equivalent amount of acetic acid equivalent with the amount of potassium hydroxide. The amounts of methanol and water are given in the table, as well as the solvolysis degrees. From example 1 it appears that with 2.5 parts by weight of water per 100 parts by weight of methanol the solvolysis in the 2nd hour still increases to 7%.

In example 2 the solvolysis appears to stop at approximately 50%. /6
By adding more water as in example 3, the solvolysis appears to stop earlier, and by adding more methanol as in example 4 the solvolysis appears to stop later. In all cases the viscosity of the solvolysis products was 20°C less than 100 cP, so that the neutralization of the catalyst can easily be carried out rapidly and homogeneously, by which polyvinyl alcohol is obtained with a small solvolysis degree distribution.

Table

example	PVAc Parts by weight	MeOH parts by weight	H_2O parts by weight	KOH parts by weight to PVAc	Solvolysis degree in mol%		
					1h	2h	3h
1	100	200	5	0.8	60	67	>70
2	100	200	10	0.8	49	50	51
3	100	200	20	0.8	41	42	43
4	100	250	10	0.8	58	60	62

CLAIMS /7

1. A method of producing polyvinyl alcohols by solvolysis of polyvinyl acetate catalyzed with alkali, wherein polyvinyl acetate is solvolyzed in a solvent mixture of an alcohol with 1-4 carbon atoms and 2-30 parts by weight of water with 100 parts by weight of alcohol to a solvolysis degree of 40-70 mol%.

2. The method according to Claim 1, wherein alcohol having 1-4 carbon atoms, methanol or ethanol, is used.

3. The method according to Claims 1-2, wherein the solvolysis is performed in a solvent mixture that contains 5-20 parts by weight per 100 parts by weight of alcohol.

4. Polyvinyl alcohol having a small solvolysis degree distribution, to be obtained according to one or more of the preceding claims.